REMARKS

Preliminarily, Applicants respectfully request the Examiner to return initialed Form PTO/SB/08 A&B (modified) for the Information Disclosure Statements filed January 12, 2006 and February 27, 2006.

Claim 1 has been amended to recite that the ferromagnetic ordered alloy phase contains CuAu type or Cu_3Au type ferromagnetic ordered particles having a substantially spherical shape. The substantially spherical-shape of the CuAu type or Cu_3Au type ferromagnetic ordered alloy particles is inherently described in the specification. Namely, when particles are produced by a reverse micelle method, the resultant particles assume a spherical shape. This is because the reaction occurs in a droplet bounded by surfactant.

Claim 2 as amended is directed to a magnetic recording medium comprising the magnetic particle-coated material of claim 1. Claim 3 as amended is directed to an electromagnetic shield material comprising the magnetic particle-coated material of claim 1 as a structural member.

The reverse micelle method as claimed in claim 13 is described at page 8, second paragraph, of the specification. The protective film of new claim 16 is described at page 35, third and fourth paragraphs of the specification.

The heat-resistant support of new claim 19 is described at page 29, lines 21 to 24. FePt is described at page 11, line 2. Si resin and PVP are described at page 32, lines 2 to 7.

Claims 4-12 directed to a non-elected invention have been cancelled. Applicants reserve the right to file a divisional application directed to the cancelled subject matter.

Entry of the amendments and review and reconsideration on the merits are requested.

Claims 1-3 were rejected under 35 U.S.C. § 102(b) as being anticipated by JP 2002-157727 (JP '727) as evidenced by Applicants' admission.

Applicants traverse, and respectfully request the Examiner to reconsider in view of the amendment to the claims and the following remarks.

JP '727 does not specifically teach the magnetic particle-coated material of amended claim 1, including CuAu type or Cu_3Au type ferromagnetic ordered alloy particles having a substantially spherical shape. In this regard, paragraph [0011] of JP '727 states that "Also, it is preferable to make the particles needle-shaped or plate-shaped by using a shape-controlling agent". Therefore, JP '727 teaches away from the use of particles having a spherical shape. The magnetic particles described in present claim 13 also have a spherical shape because they are produced by a reverse micelle method. See Hattori et al, "Synthesis of FePt and FePtCu Nanoparticles by a Reverse Micelle Method and Studies of Magnetic Recording Media Using Them", Trans. Magn. Soc. Japan, 4, 85-88 (2004), copy attached.

JP '727 also does not teach or suggest a protective film formed on the magnetic layer as claimed in independent claim 16.

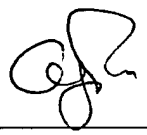
JP '727 also does not disclose the specific combination of independent claim 19, and does not teach or suggest the desirability of such combination.

Withdrawal of all rejections and allowance of claims 1-3 and 13-26 is earnestly solicited.

In the event that the Examiner believes that it may be helpful to advance prosecution of this application, the Examiner is invited to contact the undersigned at the local Washington, DC telephone number indicated below.

The USPTO is directed and authorized to charge all required fees, except for the Issue Fee and the Publication Fee, to Deposit Account No. 19-4880. Please also credit any overpayments to said Deposit Account. A duplicate copy of this paper is attached.

Respectfully submitted,



SUGHRUE MION, PLLC
Telephone: (202) 293-7060
Facsimile: (202) 293-7860

WASHINGTON OFFICE
23373
CUSTOMER NUMBER

Abraham J. Rosner
Registration No. 33,276

Date: March 27, 2006

Trans. Magn. Soc. Japan, 4, 85–88 (2004)

Synthesis of FePt and FePtCu Nanoparticles by a Reverse Micelle Method and Studies of Magnetic Recording Media Using Them

Y. Hattori*, K. Waki**, K. Ogawa**, and G. Furusawa**

*Research Laboratories for Recording Media, Fuji Photo Film Co., Ltd.

Ohgi-cho, Odawara, Kanagawa 250-0001, Japan

**Advanced Core Technology Laboratories, Fuji Photo Film Co., Ltd.

Minamiashigara, Kanagawa 250-0193, Japan

Nanoparticulate FePt, which is highly stable under heating, is a very promising magnetic material for future super-high-density magnetic recording media. The FePt and FePtCu nanoparticles were synthesized by a reverse micelle method (H_2O/sodium bis (2-ethylhexyl) sulfosuccinate (AOT)/decane). FePt and FePtCu nanoparticles obtained with this method exhibited monodispersity and homogeneous elemental composition (both coefficients of variation are less than 10%), and the average diameter of these particles was able to arbitrarily controlled between 3 and 9 nm. Further, annealing of the FePtCu nanoparticles in an $Ar+H_2$ (5%) gas lowered the temperature for modification from fcc to fct by way of the oxidation state to the range of 350°C-375°C. Nanoparticulate FePt and FePtCu media coated on glass substrates had a surface roughness (Ra) of less than 1 nm and showed magnetic recording capability.

Key words: magnetic recording, hard magnetic material, nanoparticle, FePt, FePtCu, reverse micelle

1. Introduction

Magnetic recording technology has made tremendous advancement in data storage density, particularly by scaling down the particles size of magnetic recording material. On the other hand, further scaling down the particles size cause super paramagnetism. The fct FePt has the smallest super paramagnetic critical size, because it has a very high magnetocrystalline anisotropy.

Sun et al. reported monodisperse FePt nanoparticles with high thermal stability, and these particles self-assemble into super lattices. And their FePt media showed magnetic recording capability[1]. Transformation temperature (transformation of the FePt from fcc to fct) was about 500°C-600°C in an N_2 gas atmosphere. And FePt nanoparticles which diameters were ca. 5nm were synthesized by a polyol process using Pt(acetylacetonate)$_2$ and toxic $Fe(CO)_5$[1].

A reverse micelle method[2] was chosen to overcome above problems. FePt nanoparticles were synthesized by a reverse micelle method using non-toxic $Fe(C_2O_4)_3(NH_4)_3$. The control of nanoparticles diameter is important for magnetic recording media provided with thermally stable magnetization. The elemental compositional homogeneity among individual FePt nanoparticles is also important because the coercivity of FePt after annealing depends on the composition[1].

A polymer substrate, which is usually used for flexible disk fabrication, does not show a high heat resistance temperature, in general. The heat resistance temperatures of aramid and polyimid are comparatively high (ca. 400°C). So, it is required to reduce the transformation temperature of FePt nanoparticles to lower than 400°C. Maeda et al. reported that FePtCu thin film showed lower transformation temperature than that of FePt thin film and also showed the possibility of the preparation of nanoparticles with a low transformation temperature.[3] In Sun's report[4], the same transformation temperature of FePtCu nanoparticles as FePt nanoparticles was indicated. In this work the fabrications of FePtCu nanoparticles and annealing condition were studied in order to lower the transformation temperature.

Meanwhile, melt cohesion of nanoparticles during annealing is not desirable for achieving a high recording density.

It is necessary to overcome several hurdles for the practical application of nanoparticulate magnetic recording media having an ultra high recording density. As a first step towards the goal, we tried to prepare a nanoparticulate magnetic recording medium. Flat surface magnetic recording media are required for spinstand measurement.

2. Experimental

2.1 Materials

$(NH_4)_3Fe(C_2O_4)_3$, K_2PtCl_6, $(NH_4)_2CuCl_4$ and sodium bis (2-ethylhexyl) sulfosuccinate (AOT) have been purchased from Wako Co Ltd..

2.2 Methods and equipments for the evaluation of nanoparticles and nanoparticulate media

The particle size was measured by Transmission Electron Microscope (TEM, JEM-2000FX by JEOL Ltd.).

The elemental composition of each nanoparticle was evaluated by Field Emission Transmission Electron Microscope and Energy Dispersive X-ray Spectroscopy (FE-TEM/EDS, HF-2200 by Hitachi Co Ltd.). The each nanoparticle was scanned by electron beam (1 nm in diameter).

The whole elemental composition was measured by Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP, ICPS-1000IV by Shimadzu Corp.) after the particles were dissolved with nitrohydrochloric acid.

The size distribution of the nanoparticles was evaluated with an image analysis system KS-300 (Carl Zwiss Co., Ltd).

The average roughness (Ra) was evaluated by Atomic Force Microscopy (AFM, NanoScopeIII by Digital Instruments Inc.). The area was 10 μm × 10 μm.

The crystal packing system was assigned by X-ray diffraction (XRD, RINT2500 by Rigaku Corp.).

The valence, the bond length and the bond order were obtained by X-ray Absorption Near Edge Spectroscopy (XANES) and Extended X-ray Absorption Fine Structure (EXAFS, R-XAS Rooper by Rigaku Corp.).

The Recording property was evaluated by Spinstand LS90 (Kyodo Denshi System Co., Ltd). The recording head used a ring head and the reproducing head used a MR head.

The magnetic properties of the media to which 70 KOe magnetic field was applied in plane with solenoid, were measured by Vibrating sample magnetometer (VSM, C7-10V by Toei Industry Co., Ltd). The maximum field of VSM was 10 KOe.

2.3 Synthesis of nanoparticles

As is schematically shown in Fig.1, reverse micelles of a metal salt and of a reductant were mixed together in an N_2 gas atmosphere. In the case of FePtCu, $(NH_4)_2CuCl_4$ was added further. In this study, nanoparticles were synthesized by a reverse micelle method (H_2O/AOT/decane). In the present reverse micelle method, a reducing reaction occurs in the water droplets. Changing the size of water droplets controls the size of the nanoparticles. The diameter of the water droplets is proportional to the H_2O/AOT mole ratio.[5-7]

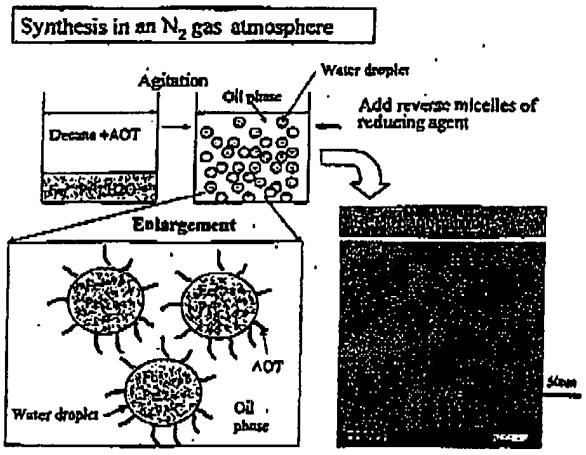


Fig.1 Preparation of FePt nanoparticles by a reverse micelle reaction and TEM image of FePt nanoparticles.

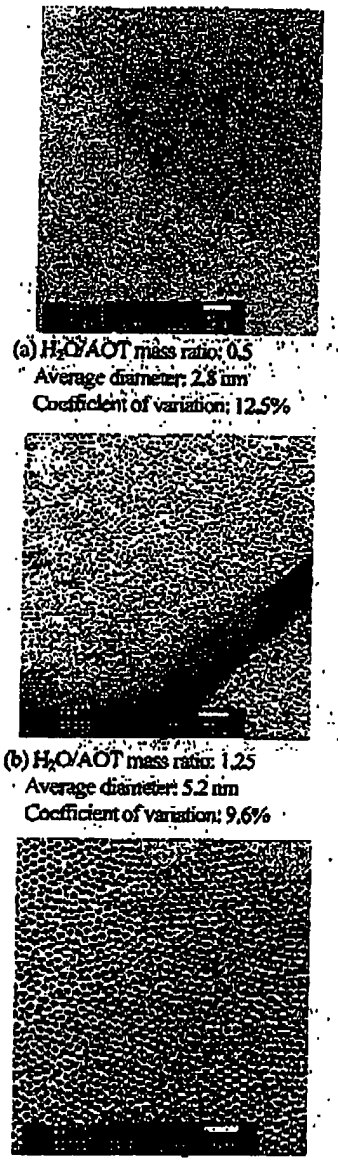
2.4 Magnetic recording media

The FePt and FePtCu nanoparticles were coated on glass substrates by a spin coater in the air. Further, via annealing of the coated product in a reducing atmosphere, a magnetic recording medium was obtained.

3.Results and discussion

3.1 Size and elemental composition of nanoparticles

Fig. 2 shows TEM images of as-synthesized FePtCu nanoparticles without classification. The average diameter of these monodisperse (with a coefficient of variation (standard deviation/average) of about 10%) nanoparticles was arbitrarily controlled between 3 nm and 9 nm.



(a) H_2O/AOT mass ratio: 0.5
Average diameter: 2.8 nm
Coefficient of variation: 12.5%

(b) H_2O/AOT mass ratio: 1.25
Average diameter: 5.2 nm
Coefficient of variation: 9.6%

(c) H_2O/AOT mass ratio: 3.0
Average diameter: 8.6 nm
Coefficient of variation: 9.2%

Fig.2 Particle size and monodispersity of the FePtCu nanoparticles.

The elemental compositions of the whole nanoparticles were $Fe_{49}Pt_{51}$ and $Fe_{46}Pt_{39}Cu_{21}$. The elemental compositions of each nanoparticulate FePt the FePtCu gave the result as $Fe_{46\pm6}Pt_{54\pm6}$ and $Fe_{34\pm5}Pt_{44\pm5}Cu_{22\pm5}$ respectively. The nanoparticles were synthesized with homogeneous compositions.

3.2 Coercivity after annealing

The relation between the annealing conditions (temperature and atmosphere) and the coercivity after annealing is shown in

Fig. 3. The magnetism of FePt nanoparticles, which were coated on a glass substrate in the air, transformed to hard from soft at around 525°C in an N_2 gas atmosphere. These results agree with those in the Sun's report[1]. In addition, the FePt nanoparticles, which were coated in an N_2 gas atmosphere transformed to hard magnetism at around 700°C in the same atmosphere. Therefore, the FePt and FePtCu nanoparticles were oxidized by air, and annealed under a reducing atmosphere. The FePt nanoparticles transformed to hard magnetism at around 400°C in an H_2 gas atmosphere. Furthermore, the FePtCu nanoparticles transformed to hard magnetism at around 350°C in the same atmosphere.

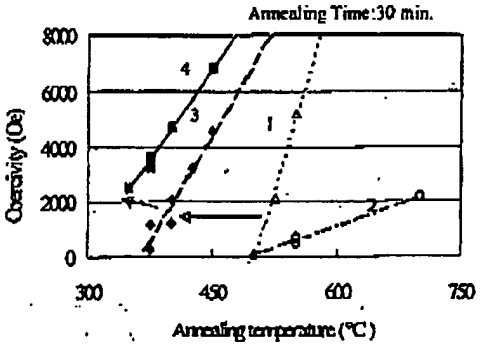


Fig.3 Effects of the annealing atmosphere and change from $Fe_{49}Pt_{51}$ to $Fe_{49}Pt_{37}Cu_{21}$ These particles diameter were about 5nm.

1: FePt coated in the air and annealed in an N_2 gas
2: FePt coated in an N_2 gas and annealed in an N_2 gas
3: FePt coated in the air and annealed in an H_2 gas
4: FePtCu coated in the air and annealed in an H_2 gas

3.3 Transformation temperature

Fig.4 shows the X-ray diffraction patterns of FePt and FePtCu nanoparticles. These particles were evaluated coercivity after annealing as described in section 3.2. The FePt nanoparticles annealed at 400°C for 30 min. in an H_2 gas atmosphere show an fct internal structure. And the FePtCu nanoparticles annealed at 350°C for 30 min. in the same atmosphere also show an fct internal structure. These transformation temperatures were lower than that of FePt nanoparticles annealed in N_2 gas atmosphere[1]. These nanoparticles were modified from fcc to fct by way of the oxidation state.

Valence of iron atom was assigned by XANES, and bond distance and bond order were estimated by EXAFS analysis. As XANES spectrum of as-synthesized FePt was similar to Fe_2O_3, most of iron atoms in as-synthesized FePt nanoparticles must be oxidized by air. (Fig. 5)

Furthermore, Fourier transform procedures in EXAFS analyses showed that each iron atom formed chemical bonds between two oxygen atoms with the bond length of 0.197nm. By annealing FePt nanoparticles in N_2 gas or H_2 gas atmosphere, iron atoms formed chemical bond with iron and platinum atoms. (Table I)

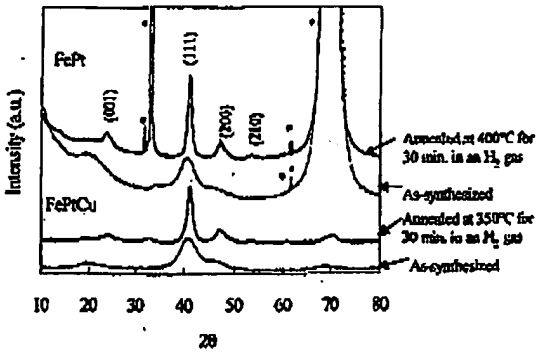


Fig.4 XRD patterns of the $Fe_{49}Pt_{51}$ and $Fe_{49}Pt_{37}Cu_{21}$ nanoparticles coated on an Si substrate (the peak (*) came from the Si substrate). These particles diameter were about 5nm.

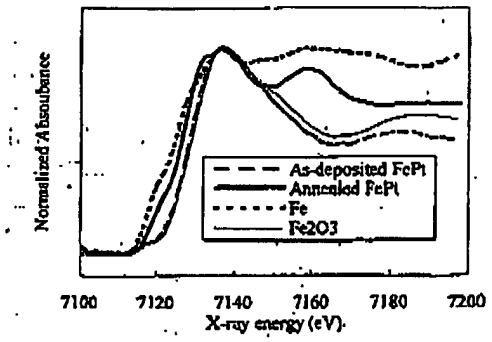


Fig. 5 XANES spectra at Fe-K edge.

Table.1 Chemical bonds of $Fe_{49}Pt_{51}$ nanoparticles.

Sample	Bond	Bond-length (nm)	Bond order
As-deposited FePt	Fe-Pt	Not detected	-
(treated in the air.)	Fe-Fe	Not detected	-
	Fe-O	0.197	2
Annealed FePt	Fe-Fe	0.264	1.4
(400°C 30 min,	Fe-Pt	0.27	3.4
in an H_2 gas)	Fe-O	Not detected	-
Fe_2O_3 standard	Fe-O	0.195	2.7
Fe standard	Fe-Fe	0.251	8.4

There was no Fe-Pt or Fe-Fe bond in the nanoparticles before the annealing. After the annealing, the nanoparticles had Fe-Pt and Fe-Fe bond. An H_2 gas has an advantage over an N_2 gas in removing oxygen from oxidized nanoparticles.

We think that the defects followed by oxygen atoms removal accelerate atomic migration, accordingly the transformation temperature lowered.

In Sun's report[4], the transformation temperature of $Fe_{55}Pt_{35}Cu_{10}$, $Fe_{45}Pt_{44}Cu_{11}$, $Fe_{44}Pt_{40}Cu_{12}$ and $Fe_{45}Pt_{40}Cu_{15}$ were 550°C-600°C. We got the same results with the $Fe_xPt_yCu_{<17}$. In the contrast, the transformation temperature of $Fe_{39}Pt_{40}Cu_{21}$ was 350°C-375°C. The average diameter of these nanoparticles was ca. 5 nm. And, we obtained the result that the range of $Fe_{35\pm14}Pt_{40\pm7}Cu_{25\pm7}$ is necessary to lower the transformation temperature.

3.4 Magnetic recording media

The magnetic recording media with the thickness of ca. 20nm were prepared using nanoparticles of ca. 5nm diameter.

The annealing condition of nanoparticulate FePt medium was 425°C for 30 min. and in the case of nanoparticulate FePtCu that was 375°C for 30 min. in an Ar+ H_2 (5%) atmosphere.

The magnetic properties and the surface roughness of magnetic recording media are given in Table 2, together with a hard disk medium. These media showed hard magnetism and had average roughness (Ra) of less than 1 nm.

No size change by annealing of nanoparticulate FePtCu was confirmed as shown in Fig. 6.

Table 2 Magnetic properties and surface roughness

	$Fe_{49}Pt_{51}$	$Fe_{49}Pt_{30}Cu_{21}$	70Gbit/in^{2}HD
Annealing	425°C 30 min. (Ar+H_2 (5%))	375°C 30 min. (Ar+H_2 (5%))	-
Hc (Oe)	2921	3259	3498
Hc (kA/m)	232	259	278
Ms (T)	0.109	0.031	0.557
Mr (T)	0.073	0.025	0.427
SR	0.67	0.81	0.77
Ra (nm)	0.87	0.55	0.5

Hc: coercivity
Ms: saturation magnetization
Mr: residual magnetization
SR: square ratio (=Mr / Ms)
Ra: average roughness

$$Ra=\left(\int_0^L |f(x)|\right)/L$$

L: length of roughness curve
f(x): deviation of roughness curve to centerline

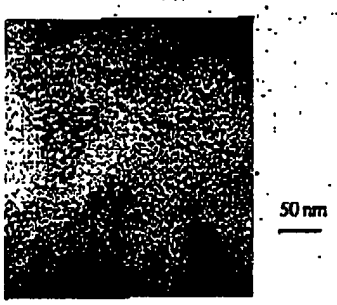


Fig.6 TEM image of the FePtCu nanoparticles removed from the medium after annealing at 400°C.

Furthermore, we wrote and read the signal at several reversal flux densities with a spinstand. The output properties of nanoparticulate FePt, FePtCu and hard disk media are shown in Fig.7. All these media exhibited magnetic recording capability. The tracking average amplitude (TAA) of nanoparticulate FePt and FePtCu media were still lower than that of hard disk media. Because of this the residual magnetization of nanoparticulate media were lower than that of hard disk media.

The output of nanoparticulate FePt medium was higher than that of the nanoparticulate FePtCu medium. It means that the Bohr magnetron of the nanoparticulate FePt is bigger than that of nanoparticulate FePtCu[8].

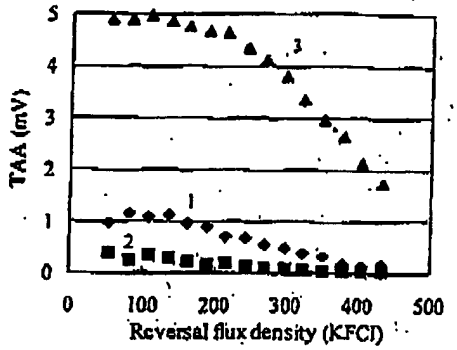


Fig.7 Output properties of FePt and FePtCu nanoparticulate magnetic media with glass substrates.

1: nanoparticulate FePt media
2: nanoparticulate FePtCu media
3: 70Gbit/in^{2}HD

4. Summary

The FePt and FePtCu nanoparticles were synthesized by employing a reverse micelle method using non-toxic iron source. They exhibited monodispersity and homogeneous elemental composition, and the average diameter of these particles could be arbitrarily controlled between 3 and 9 nm.

The FePtCu nanoparticles in a reducing atmosphere lowered the temperature for modification from fcc to fct by the oxidation state to the range of 350°C -375°C.

Magnetic recording media were prepared having average roughness (Ra) of less than 1 nm and showing a magnetic recording capability measured with a spinstand.

The magnetic recording property must be influenced by the composition of element in the particle.

Acknowledgments We thank to Dr. Taguchi and Rigaku Corp. for their great support on XANES and EXAFS analysis.

References

1) S. Sun, C. B. Murray, D. Weller, L. Folks, A. Moser: Science, 287, 1989-1992 (2000).
2) M. P. Pileni: "Structure and Reactivity in Reverse Micelles", Elsevier Science Publishers B.V. (1989)
3) T. Maeda, T. Kai, A. Kikitsu, T. Nagase, J. Akiyama: Appl. Phys. Lett., 80, 2147 (2002).
4) X. Sun, S. Kang, J. W. Harrell, D. E. Nikles, Z. R. Dai, J. Li, Z. L. Wang: J. Appl. Phys, 93, 7337 (2003).
5) K. Hamada, K. Hatanaka, T. Kawai, K. Kon-no: SHIKIZAI, 73 (8), 385-390 (2000).
6) M. Wu, D. Chen, T. Huang: Langmuir, 17, 3877-3883 (2001).
7) K. Tajima, Y. Imai: KAGAKU KOGYO, March, 175-181 (2001).
8) T. Kai, T. Maeda, A. Kikitsu, J. Akiyama, T. Nagase, T.Kishi: J. Appl. Phys, 95, 609 (2004).

Received Apr.16, 2004; Accepted Jun.16, 2004.